Structural and Magnetic Properties of Trigonal Iron

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Abstract

First principles calculations of the electronic structure of trigonal iron were performed using density function theory. The results are used to predict lattice spacings, magnetic moments and elastic properties; these are in good agreement with experiment for both the bcc and fcc structures. We find however, that in extracting these quantities great care must be taken in interpreting numerical fits to the calculated total energies. In addition, the results for bulk iron give insight into the properties of thin iron films. Thin films grown on substrates with mismatched lattice constants often have non-cubic symmetry. If they are thicker than a few monolayers their electronic structure is similar to a bulk material with an appropriately distorted geometry, as in our trigonal calculations. We recast our bulk results in terms of an iron film grown on the (111) surface of an fcc substrate, and find the predicted strain energies and moments accurately reflect the trends for iron growth on a variety of substrates.

75.50.Bb, 75.70.-i, 75.20.En

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I. INTRODUCTION

Thin transition metal films can be grown on a variety of substrates. The position of the atoms in the first film layer is largely determined by the surface geometry of the substrate. As more layers are added the lattice geometry of the film is determined by the forces at the substrate interface and by the inter-atomic forces within the film. As the film gets even thicker its geometry will eventually become that of the stable bulk material. Films with just a few layers give us the opportunity to study transition metals in geometries other than that of the bulk material, but with the additional complication of a interface with the substrate. Electronic structure calculations that include the effects of the substrate interface have revealed that other than the imposition of a non-bulk lattice geometry throughout the film, only the interface layer of the metal film is strongly affected by the substrate.[1] As a result bulk electronic structure calculations which ignore the details of the interface interactions but which use lattice constants characteristic of the substrate should give a good picture of the thin film electronic structure.

Thin films of iron can be grown on substrates with a variety of lattice constants, so a range of calculations, corresponding to several different distortions of the bulk structure, are necessary to characterize these films. A distortion of a cubic unit cell along the (111) axis can be examined using a trigonal basis. The trigonal basis, characterized by three equal length vectors originating at the origin and the equal angle which separates each of them, contains the bcc, fcc, and simple cubic structures as special cases. By varying the characteristic angle one can obtain these special geometries and the distortion along the (111) axis which connects them. Electronic structure calculations of distorted structures near the bcc and fcc geometries will allow us to extrapolate elastic constants for these bulk geometries. More importantly in this context, these trigonal structures are exactly those which match the lattice provided by the (111) face of an fcc substrate. So an electronic structure calculation of bulk iron with a trigonal geometry gives us insight into iron films grown on these substrates. Similarly, a tetragonal unit cell provides the correct distortion

to match the (100) face of a cubic substrate.[2]

In this brief report we will give the results of electronic structure calculations for ferromagnetic bulk iron over a range of trigonal geometries. The full-potential linearized augmented plane wave method (FLAPW) was used with Janak's parametrization of von Barth and Hedin's local density approximation to the exchange and correlation potential.[3,4] Some refinement of results from similar previous calculations for a tetragonal geometry will also be presented.[2]

II. RESULTS FOR BULK MATERIALS

Figure 1 shows the range of lattice geometries over which the energy calculations were performed. For this one atom per unit cell trigonal structure the geometry is parameterized in terms of the c/a ratio and the volume per unit cell. The natural log of the c/a ratio is used since it provides a more natural scaling. The volume is scaled by the experimental bcc volume (78.83 a.u.). The three special geometries, fcc, simple cubic, and bcc, correspond to ln(c/a) values of 0.69, 0.0 and -0.69 respectively. Geometries at which electronic structure calculations were performed are indicated by a dot. Using the total energy result at each of these points we can numerically construct constant energy contours as shown in figure 1.

The most prominent features in this contour plot are the two local energy minimas corresponding to an fcc and a bcc structure. As has been observed in previous calculations the global minima is mispredicted; the fcc structure lies about 4 mRyd low than the bcc structure. At lower temperatures iron is actually a bcc crystal so we would expect a bcc structure to appear as the global minima for these calculations. This error is widely attributed to the inherent inaccuracy of the specific form of the local density approximation we have used.[5] One can travel between these two locally stable structures by varying the c/a ratio, which corresponds to distorting either cubic structure along the (111) axis. The energy barrier between bcc and fcc structures for this distortion is approximately 70 mRyd/atom, significantly larger than the 10 mRyd/atom found for the tetragonal distortion which connects

the bcc and fcc structures.[2]

The data near the two minima can be used to obtain lattice constants, volumes and elastic properties of these two high symmetry structures. Ideally one would investigate regions extremely close to the energy minima where the energy varies quadratically with small distortions in the geometry. In this case a simple quadratic fit would perfectly model the behavior of the electronic energy around the minima allowing the various crystal properties to be extracted with great reliability. Unfortunately, because of the limited accuracy in the calculated energies, we need to look at structures further from the minima to ensure the energy differences among our structures are larger than the background numerical noise. As a result, we can no longer expect a simple quadratic fit to perfectly model variation in total energy among the structures near the minima.

To account for this inherent inaccuracy the data were fit by a number of methods. Two dimensional fits of energy versus volume along the fcc ($\ln(c/a) = 0.69$) and bcc ($\ln(c/a) = -0.69$) lines were performed with a simple quadratic model as well as with the Murnaghan and Birch-Murnaghan models.[6] Three-dimensional quadratic fits were made to points near the minima in the c/a versus V plane. The particular points to which each model was fitted were varied and the sensitivity of the final results to these variations was noted. In all cases 'good' (in terms of Chi-squared) fits were obtained. The variation in results between the different fits was used as an estimate of the uncertainty introduced by the use of imperfect fitting models. The lattice constants and volumes obtained were consistent for the various fitting techniques. The elastic constants showed some variation, especially for the fcc minima. The elastic constants obtained from the three-dimensional quadratic fit were especially sensitive to the selection of fitted points. Tables I and II show some sample results from a variety of fits done near the bcc and fcc minima. Considered carefully, the fitting errors are no greater than those known to be inherent in the local density approximation: 2-3% in the lattice constants and 10-20% in the elastic constants.

Combining these fit results and similar results from a refitting of previous calculations on tetragonally distorted iron, we obtained the predicted bulk ferromagnetic iron properties

shown in table III.[2] Along with our results, table III gives experimental numbers for these properties along with the results from other density functional calculations.[7,8] The numbers for the bcc minima are in good agreement with the other theoretical predictions (also done under the LDA) consistently underestimating the lattice constants by a few percent, and over-estimating the elastic properties by a few tens of percent. For the fcc data we present theoretical numbers from the so called 'low-spin' ferromagnetic state and experimental results from gamma-iron, the high temperature fcc phase. The discrepancy between theory and experiment is larger in this comparison, which is expected since the theoretical calculations do not take temperature fully into account. In both the fcc and bcc case the large values for the elastic constants can be largely attributed to the underestimate of the lattice constant. In general one finds in LDA calculations that the smaller the equilibrium volume, compared to the experimental value, the larger the bulk modulus. If we were to force the unit cell volume to be closer to the experimental value we could obtain elastic properties closer to those experimentally measured.

III. RELATION TO THIN FILMS

As was mentioned above, these bulk results can be related to thin iron films by recasting the data in terms of iron grown in perfect registry with the (111) surface of an fcc substrate. In figure 2 we show a contour plot of the same data as figure 1, but now it has been parameterized in terms of a film geometry. The in-plane lattice spacing in the film will be fixed by the substrate since we assume the film is grown pseudomorphically. The interlayer spacing will take on whatever value minimizes the energy for the given in-plane spacing. If we know the lattice constant of our substrate we can immediately extrapolate from figure 2 the interlayer spacing that minimizes the energy. Following this procedure for a range of substrate lattice constants we construct figure 3 which shows the energy of the film with optimal interlayer spacing as a function of the substrate lattice constant. The left and right minima in this figure correspond to unstrained fcc, and unstrained bcc growth

respectively. The energy shift near these minima can be interpreted as the strain energy per layer associated with strained, pseudomorphic growth.

As shown in figure 4 we can, following a similar procedure, express the results of our bulk magnetic moment calculations as a function of substrate lattice constant, again with optimal interlayer spacing. In this figure we can see that unstrained fcc films have small moments, but increasing the substrate lattice constant causes the moment to rise. In the region of bcc growth the moment is not particularly sensitive to changes in the substrate. Keep in mind that these results ignore the interface effects which play a key role in the magnetic properties of such films.

With this caveat in mind we can relate these figures to the observed properties of thin iron films for a variety of substrates. Copper, with an fcc lattice constant of 6.82 a.u. should provide a reasonable match for pseudomorphic growth of iron films. Figures 2, 3, and 4 predict iron grown on copper (111) is a strained fcc structure with an interlayer spacing of around 3.7 ± 0.2 a.u. and a moment of 1.0 ± 0.25. Recent studies showed strained fcc growth up to five layers with interlayer spacings of 3.9 a.u. and moments of $1\mu B$/atom consistent with our result.[9,10] Less well matched substrates have been studied as well. Using Pd , which has a lattice constant of 7.36 a.u., as a substrate should create a strain energy per layer nearly twice that of copper according to figure 3. Not surprisingly it was found that less than two layers of iron could be grown pseudomorphically on Pd before islands of bcc iron started to form.[11] Substrates which would provide even larger strains than Pd, namely Ag and Al do not appear to give clean pseudomorphic growth as expected from figure 3.[11]

IV. CONCLUSIONS

In this paper we have examined a range of trigonal iron structures using density functional theory. We find energy minima corresponding to the expected bcc and fcc geometries. While carefully considering the inherent inaccuracy in the fitting process we can extract information about the properties of these bulk states which are in good agreement with

experimental results. We also recast the bulk results to reflect the geometries associated with the pseudomorphic growth of thin iron films. Although this approach ignores the interface and surface effects it still gives meaningful insight into the growth of iron films on a range of substrates. The predicted film properties are consistent with the growth observed for a variety of substrates.

ACKNOWLEDGMENTS

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FIGURES

FIG. 1. Contours of constant energy (mRyd/atom) of ferromagnetic trigonal iron as a function of volume and c/a ratio. Dots indicate geometries at which electronic structure calculations were performed. All energies are offset by 2541 mRyd.

FIG. 2. Contours of constant energy (mRyd/atom) of a ferromagnetic iron film as a function of fcc substrate lattice constant and film interlayer spacing. Dots indicate geometries at which electronic structure calculations were performed. Contours far from data points are unreliable. All energies are offset by 2541 mRyd.

FIG. 3. Energy (mRyd/atom) of a thin iron film with optimal interlayer spacing as a function of the fcc substrate lattice constant. All energies are offset by 2541 mRyd. A line is provided to guide the eye.

FIG. 4. Magnetic moment (μB/atom) of a thin iron film with optimal interlayer spacing as a function of the fcc substrate lattice constant.

TABLE I. Properties of bcc iron as predicted by a variety of fitting models.

c/a	Volume (a.u.)	Energy (mRyd.)	Bulk Modulus (Mbar)	Fitting Method
0.5	73.4	-0.103	2.25	parabola to 4 points
0.5	71.9	-0.102	1.77	Murnaghan near minima
0.5	73.3	-0.103	2.30	Birch-Murnaghan near minima
0.5	71.1	-0.103	2.19	Murnaghan over full range of V
0.5	71.2	-0.104	2.33	Birch-Murnaghan over full range of V
0.5084	73.2	-0.101	2.11	3-d quadratic with minimum error
0.5092	73.1	-0.101	2.14	3-d quadratic with average error
0.5101	73.1	-0.102	2.22	3-d quadratic with average error

TABLE II. Properties of fcc iron as predicted by a variety of fitting models.

c/a	Volume (a.u.)	Energy (mRyd.)	Bulk Modulus (Mbar)	Fitting Method
2.0	65.8	-0.105	3.19	parabola to 4 points
2.0	65.9	-0.109	3.09	Murnaghan near minima
2.0	65.7	-0.105	3.16	Birch-Murnaghan near minima
2.0	66.0	-0.103	2.20	Murnaghan over full range of V
2.0	65.6	-0.104	2.57	Birch-Murnaghan over full range of V
2.023	67.2	-0.107	3.66	3-d quadratic with minimum error
2.006	66.9	-0.111	3.74	3-d quadratic with average error
2.014	66.9	-0.103	2.30	3-d quadratic with average error

TABLE III. Properties of bcc and fcc iron. Results from this study and other density functional calculations, as well as experimental results for α-iron and γ-iron. All elastic properties are in Mbar.

	lattice constant (a.u.)	moment (μB)	Bulk Modulus	c_{11}	c_{12}	c_{44}
bcc						
theory	5.24 ± 0.1	2.0 ± 0.05	2.2 ± 0.15	2.9 ± 1.1	1.8 ± 0.6	1.5 ± 0.3
theory[a]	5.21	2.08	2.66			
exper.[b]	5.406	2.12	1.68	2.33	1.355	1.178
fcc						
theory	6.43 ± 0.1	0.0	2.6 ± 0.4	5.4 ± 1.0	1.2 ± 0.3	2.6 ± 0.6
theory[c]	6.37	0.0	3.9			
exper.[d]	6.947	0.0	1.32	1.54	1.22	0.77

[a]from Ref. 8

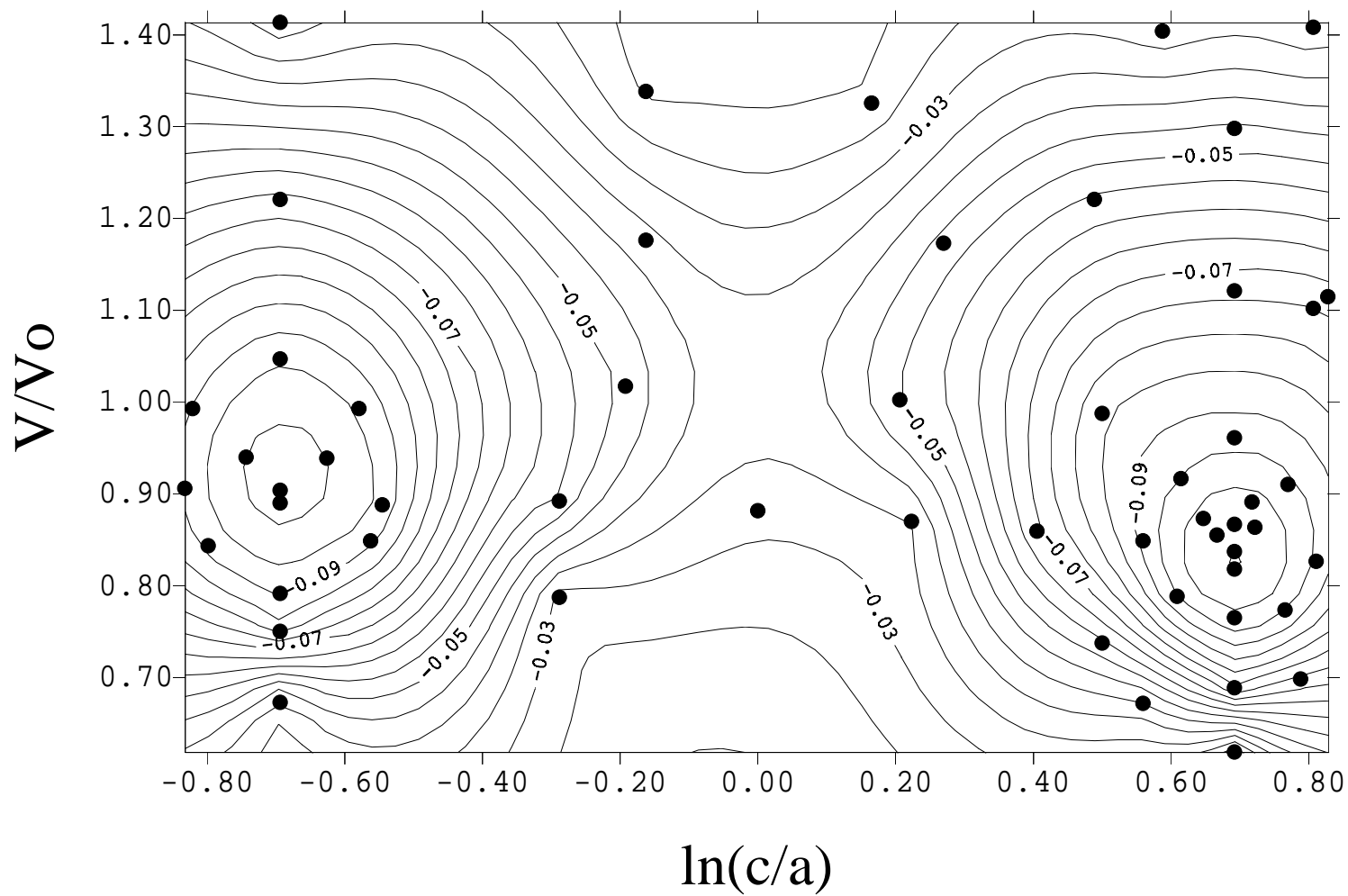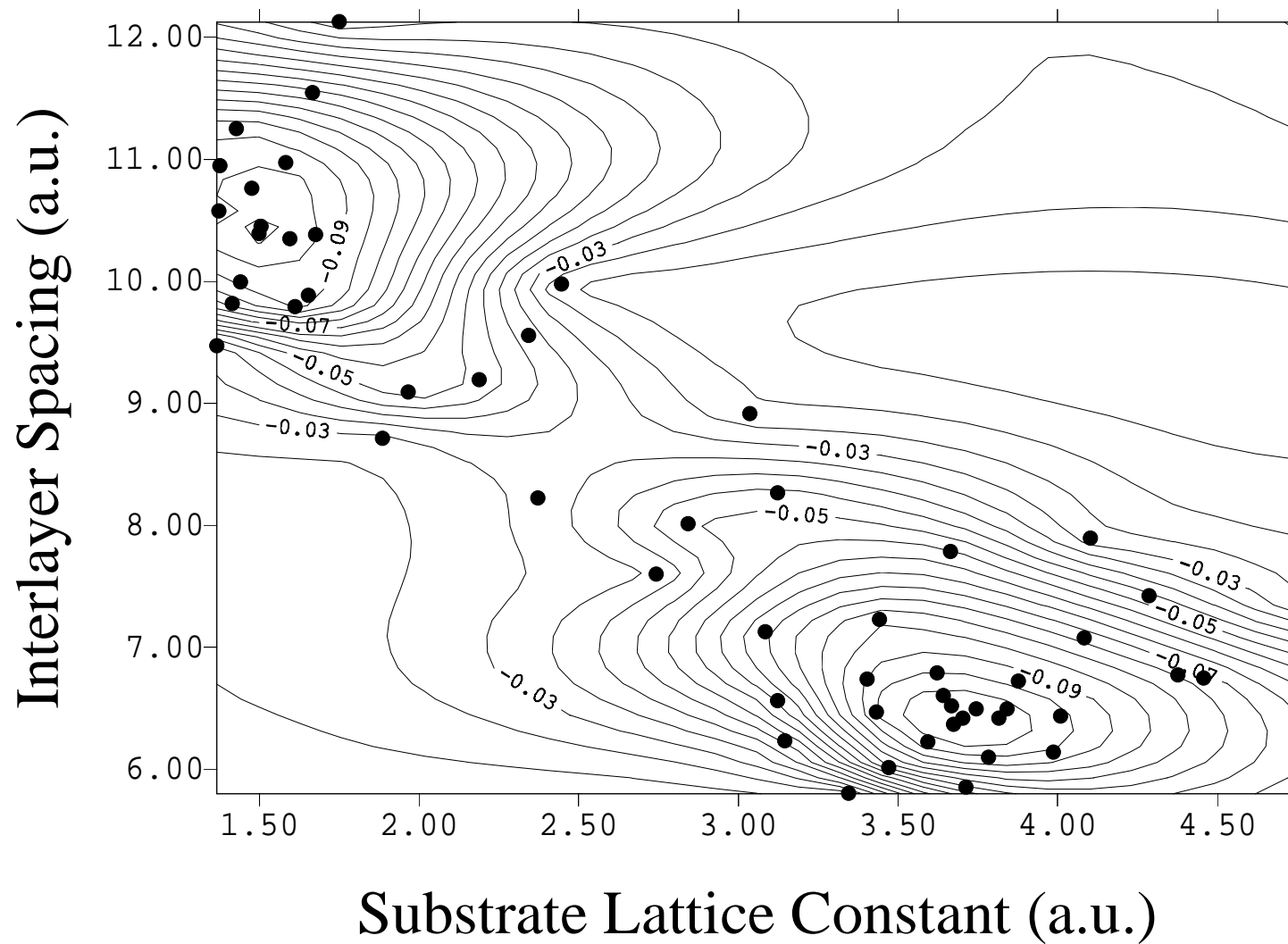[b]α-iron from Ref. 7

[c]Low-Spin results from Ref. 8

[d]γ-iron from Ref. 7

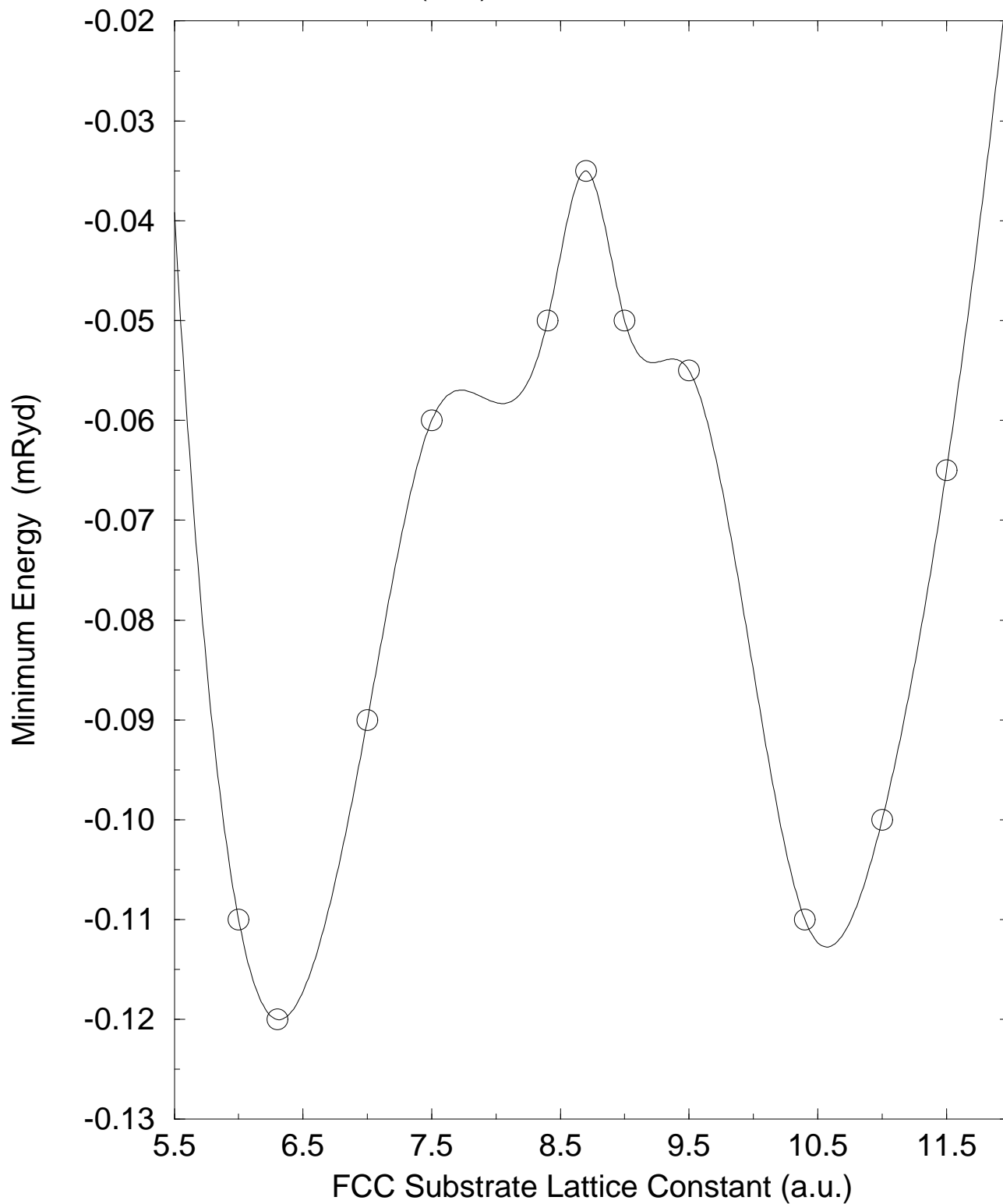# Trigonal Iron -- Constant Energy Contours

Fe Growth on (111) Surface of FCC Substrate

Energy with Optimal Interlayer Spacing

Fe on (111) Surface of FCC Substrate

Magnetic Moment with Optimal Interlayer Spacing

Fe on (111) Surface of FCC Substrate